Supplementary Information

Synthesis of environmentally friendly energetic cocrystal derived from commodity chemicals

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Experimental

Ammonium nitrate (AN) and sarcosine (Sar) were purchased from Fujifilm Wako Pure Chemical Corporation and Tokyo Chemical Industry Co. Ltd., respectively. Glycine (Gly) was obtained from Kanto Chemical Co., Inc. (for the humidity test) and Fujifilm Wako Pure Chemical Corporation (for all other experiments).

Single-crystal X-ray diffraction was performed using an XtaLAB PRO (RIGAKU). A Cu Kα radiation source was used at 50 kV and 0.6 mA. H atoms were found in differential fourier map and refined isotopically. Computer programs: CrysAlis PRO 1.171.40.66a[1], SHELXT[2] 2018/2, SHELXL[3] 2018/3, Olex2 1.5[4], Mercury[5], and publCIF[6]. DSC (Q200, TA Instruments) was used under a 50 mL flow of N_2. The SUS-sealed cell was heated at 10 K/min. Cyclic DSC analysis was performed using the following temperature program: Isotherm at 30 °C, ramp up to 120 °C, ramp down to 20 °C, ramp up to 120 °C, ramp down to 20 °C, and ramp up to 350 °C; the heating rate was set to 5 K/min. TG-DTA was performed using a Thermoplus TG8120 (RIGAKU) instrument with an Al_2O_3 open cell. The sample was heated at a rate of 10 K/min under a 50 ml N_2 flow.

Fourier-transform infrared (FT-IR) spectroscopy was performed using an FT-IR 6200 spectrometer (JASCO). The Attenuated Total Reflection (ATR) method was applied using a ZnSe prism. Cocrystal samples prepared by the cooling method were used for FT-IR measurements. Powder X-ray diffraction (XRD) was performed using a Smart Lab instrument (RIGAKU). The scan rate was set at 20° 2θ min^{-1} at 40 kV and 45 mA. Elemental analysis (EA) was conducted using a UNICUBE instrument (Elementar Analysensysteme GmbH). The amount of AN/Gly prepared by the cooling method was measured.

Trials to form AN cocrystal with the other amino acids

Alanine and Arginine were selected from the viewpoints of O. B and availability. AN and alanine (Tokyo Chemical Industry Co. Ltd.) were dissolved in deionized water, and the solution was cooled at 4 °C. Single crystals were obtained over two days, but they were pristine alanine crystals and cocrystals were not detected. AN and arginine (Fujifilm Wako Pure Chemical Corporation) were ground using a motor and pestle adding a small amount of water. The product was analyzed using P-XRD, and the results suggested the formation of L-argininium nitrate hemihydrate (CCDC: 1215602)[7].

Table S1 Crystal data for AN/Gly.

Crystal data	
Chemical formula	$C_2H_5NO_2 \cdot 2(NO_3) \cdot 2(NH_4)$
M_r	235.17
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	223
a, b, c (Å)	5.7762(1), 22.1425(4), 7.9135(1)
β (°)	92.015(2)
V (Å^3)	1011.51(3)
Z	4
Radiation type	Cu Kα
μ (mm^{-1})	1.38
Crystal size (mm)	0.15 × 0.1 × 0.1
Data collection	
Diffractometer	XtaLAB AFC12 (RINC): Kappa dual offset/near
Absorption correction	Multi-scan
T_{min}, T_{max}	0.758, 1.000
No. of measured, independent and observed [I > 2σ(I)] reflections	5369, 2007, 1803
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.627
Refinement	
R[F^2 > 2σ(F^2)], wR(F^2), S	0.033, 0.095, 1.07
No. of reflections	2007
No. of parameters	189
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, -0.16

Table S2 Hydrogen bonds geometry for AN/Gly and AN (IV) (Å, °)[8].

	D…A	D-H	H…A	D-H…A
AN/Gly				
N2-H2A...O2	2.838 (2)	0.90 (2)	1.97 (2)	162.38 (2)
N2-H2B…O2	2.873 (2)	0.91 (2)	2.00 (2)	161.30 (2)
N2-H2C…O5	2.963 (2)	0.83 (2)	2.14 (2)	168.52 (2)
N2-H2D…O3	2.916 (2)	0.91 (3)	2.05 (3)	159.81 (2)
N4-H4A…O1	2.833 (1)	0.93 (2)	1.91 (2)	171.32 (2)
N4-H4B…O6	2.910 (2)	0.89 (3)	2.03 (3)	171.48 (2)
N4-H4C…O7	3.056 (2)	0.88 (3)	2.23 (3)	157.18 (2)
N4-H4D…O1	2.867 (2)	0.85 (3)	2.22 (3)	133.54 (2)
AN (IV)				
N1-H1...O1	2.971	0.987	2.050	154.42
N1-H2…O2	2.935	0.992	2.637	97.93

Table S3 Elemental analysis results for AN/Gly.

	C (%)	N (%)	H (%)
Measured	29.75	9.75	5.53
calculated	29.77	10.21	5.53

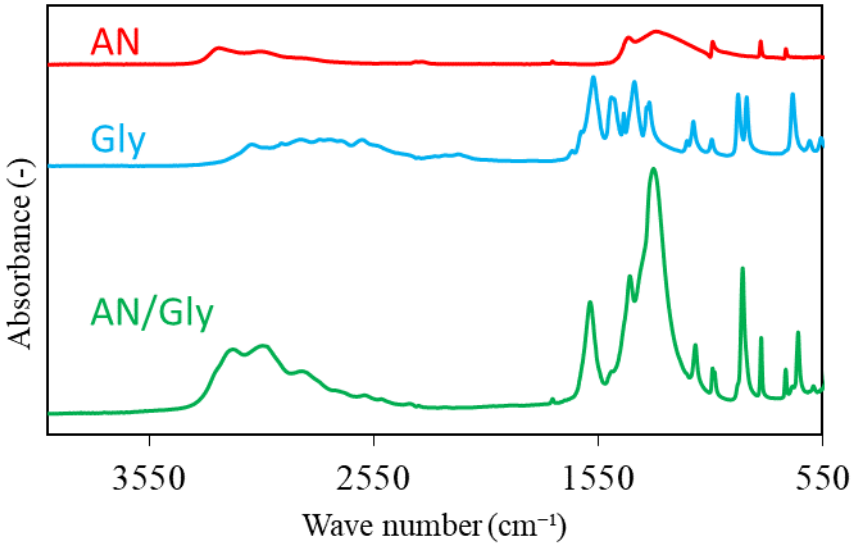

Figure S1. Results of Fourier-transform infrared spectroscopy.

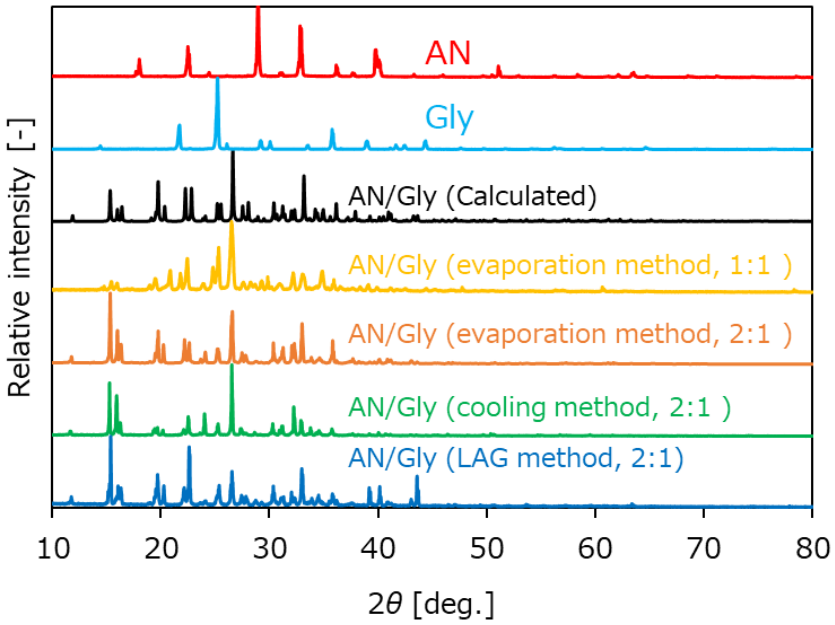

Figure S2. Results of powder X-ray diffraction. All three preparations were conducted using deionized water. Preparations by evaporation method were performed at two types of ratio: AN:Gly = 1:1 and 2:1.

The P-XRD results for AN/Gly (evaporation method, 1:1) showed unknown peaks at 20.9°, 24.7°, and 29.9° and peaks derived from pristine Gly at 21.8° and 33.4°. However, the spectra of AN/Gly prepared by the evaporation (AN:Gly = 2:1), cooling, and LAG methods corresponded to the calculated values.

Reference

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